



Characterization of the reactive system involved in the high temperature treatment of tar and gas coming from biomass pyrolysis

Françoise Nozahic, Méryl Brothier, Xuân-Mi Meyer, Xavier Joulia, Christian Latgé

► To cite this version:

Françoise Nozahic, Méryl Brothier, Xuân-Mi Meyer, Xavier Joulia, Christian Latgé. Characterization of the reactive system involved in the high temperature treatment of tar and gas coming from biomass pyrolysis. 1st International Congress on Green Process Engineering (GPE 2007), Apr 2007, Toulouse, France. pp.0. hal-04106622

HAL Id: hal-04106622

<https://hal.science/hal-04106622>

Submitted on 25 May 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Characterization of the reactive system involved in the high temperature treatment of tar and gas coming from biomass pyrolysis

NOZAHIC Françoise^a, BROTHIER Meryl^b, MEYER Xuân-Mi^a, X. JOULIA Xavier^a, LATGE Christian^b

^a Laboratoire de Génie Chimique
5 rue Paulin Talabot - BP 1301
31106 Toulouse cedex 1 – France

Françoise.Nozahic@ensiacet.fr ; Xuan.Meyer@ensiacet.fr

^b Commissariat à l'Énergie Atomique – Cadarache – DTN/STPA/LPC
13108 Saint Paul-lez-Durance cedex – France
Meryl.Brothier@cea.fr

Abstract

This work contributes to the on going emergence of new technologies for energy production. It deals with the use of lignocellulosic biomasses to produce syngas that can be transformed into synthetic fuel by the Fischer Tropsch process. A two-stage process is studied performing first the biomass pyrolysis then the catalytic treatment of the produced gas at 1000°C. The objective of this study is to better understand the physical and chemical phenomena involved during the high temperature gas treatment stage through a coupled experimental and modelling approach. A particular attention is paid to the removal of tar produced during the first stage, and to the opportunity of using the char produced during the biomass pyrolysis as catalyst in the second stage.

A phenomenological model describing the system (geometry, heat transfer, mass transfer between the different phases (gas, tar, char) and throughout the bed) has to be developed. The tar and the char compositions and potential interactions are particularly complex. Indeed, the tar is a lump of a hundred compounds and in addition, the reaction network is rather complex: decomposition reactions (steam and dry reforming, cracking), polymerisations, soot formation and interactions between the compounds. So some “model compounds” illustrating some of the characteristics of the whole group or the limit of these characteristics (i.e. the steam reforming reactivity, the thermal stability...) have been selected to simplify the reaction network.

In order to establish the basis of the phenomenological model, some preliminary experiments are carried out on the Biocarb facility to study the behaviour of the first stage and the destruction of tar on different loads.

Key-words: Biomass – Pyrolysis – Tar – Syngas - Char

1. Introduction

Nowadays, the increasing cost of the oil and the general wish to decrease the CO₂ production, in particular from the transport and also to restrict the greenhouse effect, lead to the development of new technologies for energy production. In this context, the use of lignocellulosic biomass is studied to produce syngas by thermochemical transformation. The syngas can be transformed into synthetic fuel by the Fischer-Tropsch process. This is known as the BTL (“Biomass To Liquid”) pathway.

The programme, induced by the “Commissariat à l'Énergie Atomique” (CEA), funded by the French Agency for Environment and Energy Management (ADEME) and CEA, and developed in cooperation with the “Laboratoire de Génie Chimique” in Toulouse, aims to produce fuel from the gasification of biomass.

The experimental device used in this study is based on a two-stage process that includes the biomass pyrolysis performed in a rotary kiln at the maximal temperature of 550°C to produce incondensable gases, tar, water and char that are described in this paper. The second stage is a high temperature treatment (at 1000°C) that has for main goal to enhance gas composition and to remove the tar with a pseudo-catalytic bed that is the char from the biomass pyrolysis.

If the syngas is used as pure hydrogen resource or reactant to be transformed into diesel by Fischer Tropsch process, its tar content must be extremely low (below 0.1 mg/Nm³). Specific works have to be achieved to control the tar production and in particular the polycyclic aromatic hydrocarbon (PAH) during the generation of syngas from various resources.

The overall objective of this study is to model the reactor designed for the treatment of the pyrolysis gas in order to understand the behaviour of the tar in contact with the char at 1000°C.

2. Experimental device

The pilot plant, named Biocarb, is represented in the Figure 1. It contains different stages: the biomass pyrolysis in a rotary kiln and the pyrolysis gas treatment in reactor named “PGTR” (Pyrolysis Gas Treatment Reactor).

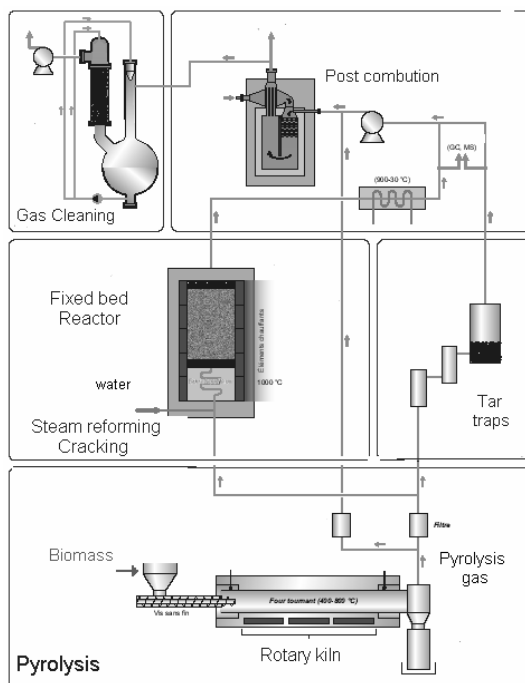


Figure 1. The "Biocarb" pilot plant scheme

2.1 Pyrolysis in a rotary kiln

The biomass pyrolysis consists of a thermal treatment with a controlled rate of heating and a given temperature in an inert atmosphere to produce a gas phase containing the incondensable gases, the condensable gases, i.e. tar and water, and a solid phase, the char.

The pyrolysis takes place in a rotary kiln that can be heated with three electrical resistances but only the one next to the exit is turned on. This allows a natural temperature profile along the kiln with a speed of heating of approximately 10°C/min. The dimensions of the pipe are 54 mm radius, 2.56 m long and the chosen rotating speed is about 3 rpm. The outlet temperature chosen from preliminary experiments is about 550°C. In addition, nitrogen is used as a co-current carrier gas for the vapours produced by pyrolysis reactions.

An endless screw that releases 600 g/h of biomass makes the continuous biomass feeding. The biomass used is wheat straw with its natural humidity near 8 % (w).

2.2 Gas treatment

This stage consists of the enhancement of the gas, i.e. the conversion of the undesirable compounds, in particular tars, methane and carbon dioxide into syngas that is a mixture of CO and H₂ at the process output.

Two devices are used to perform this stage.

The first device is the “PGTR” where the gases fed continuously from the pyrolysis i.e. the incondensable gases, the water and the tar that are gaseous at these temperatures. An electric super heater heats these gases before they enter the reactor and the temperature can reach 1000°C. It is 880 mm height with 150 mm diameter while the bed is 480 mm height and 150 mm diameter. This reactor can be filled with inert components or catalyst or with char as it is shown in the Figure 2.

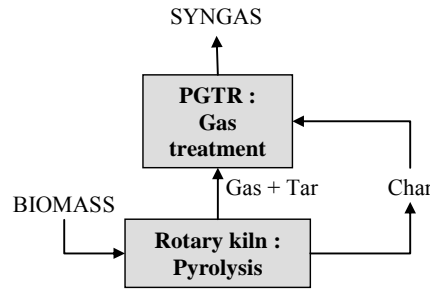


Figure 2. Use of all pyrolysis products in the PGTR

The second device is a high temperature line consisting of two furnaces put in series with only one tube in ceramic. The first furnace is heated at 1200°C and the second one is heated up to 1400°C, which is the theoretical temperature for the total destruction of the tar.

3 Exploratory approach

The biomass pyrolysis generates four different kinds of products: incondensable gas and water, referred as “gas”, and tar and char in different proportions according to in particular the rotation speed, the temperature, the heat rate, the residence time during the pyrolysis and the kind of biomass in the rotary kiln. In this study, only results concerning wheat straw are exposed.

3.1 Gas

3.1.1 Composition

The permanent gas is a mixture of CH₄, CO, CO₂, C₃H₈, H₂ and H₂O. The composition of the gas depends of the pyrolysis conditions. The composition presented on the Table 1 corresponds to the pyrolysis of wheat straw presented in the experimental description.

Table 1. Molar composition of the gas out of the pyrolysis

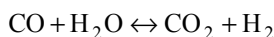
H ₂	CH ₄	CO	CO ₂	H ₂ O	N ₂
6.8 %	4.3 %	9.0 %	13.4 %	15.7 %	50.8 %

The water out of the pyrolysis comes from the natural moisture of the biomass and from the reactions taking place in gas phase during the pyrolysis.

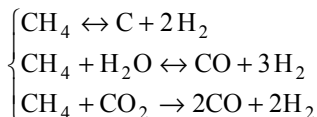
The nitrogen is used as carrier gas to extract the gases resulting from pyrolysis from the rotary kiln.

3.1.2 Reactions

The reactions to be taken into account within the gas phase are the reaction of water gas shift:



and the reactions associated to the methane degradation that can not be neglected because of its high stability at this temperature level:



Different compounds can catalyse these reactions. In particular, mixtures of olivine or dolomites with Nickel, studied by Courson et al. (2002) and by Pfeifer et al. (2004), show a strong catalyst activity on the vapour or dry reforming of methane at temperatures ranging from 750 to 900°C.

3.2 Tar

3.2.1 Definition

The tar is a lump of more than one hundred hydrocarbons with a molecular weight higher than that of benzene. The compounds can be linear, cyclic, aromatic or polycyclic aromatic.

3.2.2 Analysis

The complexity of the tar lump compels us to carry out four methods of analysis:

- The solid phase microextraction (SPME). This is a solvent-free method of extraction that combines sampling, extraction, concentration and introduction of the sample in the chromatograph in a single step (Guehenneux et al., 2002). A syringe that contains a fibre of polymer collects tars and then it is inserted directly in a gas chromatograph.
- The SPA method (solid phase adsorption). The principle is that a sorbent tube traps tar compounds from the gaseous phase with a silica-bonded amino-phase at ambient temperature (Brage et al., 2000). This method is under investigation in our laboratory.
- The two cold traps. The first is a modular sampling train based on the European protocol (Simell et al., 2000) and improved by experience feedback. The tar is condensed and injected in a gas chromatograph. But this method has a tar concentration limit in the gas of 50 to 100 mg/Nm³ and this limit is higher than the minimum concentration required. The second trapping installed on the Biocarb is a dry one. It consists of two droplet catchers that are two plate heat exchangers of which the cooling liquid is water with glycol at a temperature close to 0 to 5°C.
- The last method is the PID (Photo-Ionisation Detector). This method gives an overall response i.e. the analyser doesn't distinguish the different compounds.

3.2.3 "Model compounds"

It is nearly impossible to take into account all the tar compounds, not only for analytical reasons but also for the too large number of reactions that should be included in the model. Different classifications have been drawn before. For example, Aznar et al. (1998) use only two families the "easy-to-destroy" or "soft" tars and the "hard-to-destroy" or "hard" tars. Milne et al. (1998) use four groups depending of the reaction regimes and Devi et al. (2005) use five groups classified by the number of cycles.

Our objective is to get an apparent reaction scheme that can represent the behaviour of the whole reactive system. So some specific compounds representative of the whole system have to be selected to represent the reactivity of the tar and also the interactions and the growth of the polycyclic aromatic hydrocarbons. They are referred as "model compounds" and have been selected on the basis of their reactivity.

First benzene was chosen because it is a common compound in biomass gasification and it is a polycyclic aromatic hydrocarbons precursor: for example two benzenes can form phenanthrene with ethylene.

The second model compound is naphthalene. It was chosen because of its presence in the condensed phase before and after the reactor of gas treatment and because of its thermal stability. By the way, it is the more studied compound in biomass gasification.

The phenol was selected because it is present at the inlet and the outlet of the reactor and that can be degraded into cyclopentadiene that can produce naphthalene.

The indene has been chosen because it is present after the reactor and it can give phenanthrene with a cyclopentadiene.

Two heavier compounds were also selected: phenanthrene, present at the reactor outlet and that can be formed by previous mechanisms and pyrene chosen as the limit between volatiles compounds and the soot.

Finally, one linear alkane, the n-pentadecane and one alkene, the 1-tetradecene were chosen because they are detected by SPME analysis and they can form benzene by ring closure.

The figure 3 shows the simplified scheme of the interactions between the different “model compounds”.

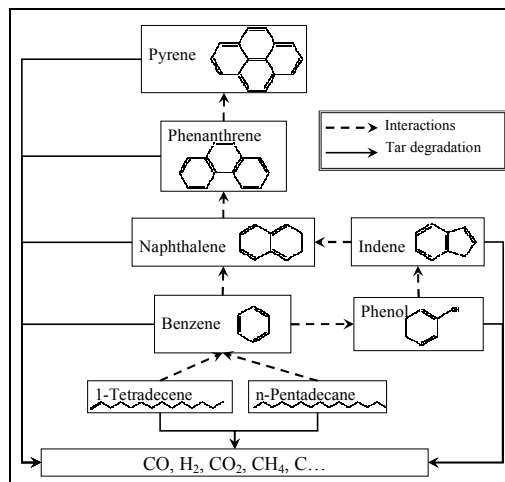


Figure 3. Simplified network of the degradation and conversion of “model compounds” of tar

All those compounds can be degraded into noncondensable gases (carbon monoxide, hydrogen, carbon dioxide and methane) and into carbon. The reactions are very numerous and only the example of naphthalene is shown here:

Vapor reforming: $C_{10}H_8 + 10 H_2O \rightarrow 10 CO + 14 H_2$

$C_{10}H_8 + 20 H_2O \rightarrow 10 CO_2 + 24 H_2$

Dry reforming: $C_{10}H_8 + 10 CO_2 \rightarrow 20 CO + 4 H_2$

Dehydrogenation: $C_{10}H_8 \rightarrow 10C + 4H_2$

Hydrocracking: $C_{10}H_8 + 16H_2 \rightarrow 10CH_4$

Carbon formation: $C_{10}H_8 \rightarrow 10C + 4H_2$

3.3 Char

3.3.1 Definition

The structure and the chemical composition of the char resulting from the biomass pyrolysis depend on the type of biomass and on the pyrolysis operating conditions i.e. the temperature level, the heating rate and the residence time.

The char can be defined at the physical level by its specific area and at the chemical level by its elementary composition, its ash content and composition because they are useful for the gas treatment.

3.3.2 Reactions

The char is assimilated to carbon and the reactions of carbon degradation taking place in the second stage are:

- The reactions of gasification with vapour: $C + H_2O \leftrightarrow CO + H_2$
- The gasification by carbon dioxide that is the inverse of Boudouard reaction: $C + CO_2 \leftrightarrow 2CO$
- The production of methane with hydrogen as reactant: $C + 2 H_2 \leftrightarrow CH_4$

4 Preliminary results

4.1 Pyrolysis in rotary kiln

Some experiments were carried out to study the pyrolysis and to try to choose the best biomass and operating conditions of the pyrolysis. Among different biomasses tested, the wheat straw has been chosen because it was not too heterogeneous and did not plug the rotary kiln.

Different temperatures were also tested: 400, 550 and 650°C. At 400°C, the gas accounts for only 10% of the mass leaving the rotary kiln whereas it constitutes approximately 40% when processing at 550°C or 650°C. The increase in temperature between 400°C and 550°C is accompanied by a rise of the ratio of H₂ and CO, and of a decrease of the quantity of water and tar. The solid content remains constant whatever the temperature.

4.2 Gas treatment

Experiments on the second stage have also been performed.

4.2.1. Temperature level

First, we have compared the output of process for two treatment temperatures with the exit of the rotary kiln that operates at a temperature reaching 550°C.

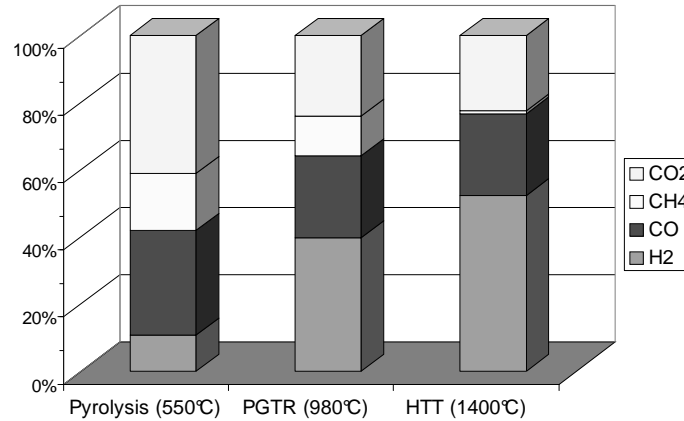


Figure 4: Molar composition of gas at different temperature levels

Compared to the results from the rotary kiln, the hydrogen content increases with temperature, it was multiplied by four at 980°C and by five at 1400°C, and the content of carbon monoxide, carbon dioxide and methane decrease.

At 1400°C the methane content is very low, near 0.85 %. Thus, as the water and the carbon are not represented on this graph and the assessment on carbon is not balanced, we can suppose that a great quantity of carbon settled down in the reactor.

Thus, the higher the temperature is, better is the gas quality but catalysts are degraded at these temperatures and in our case, the char would be gasified too quickly.

4.2.2. Catalysts

Then the performance of different catalysts was evaluated. The composition in the incondensable gas at the “PGTR” outlet for the different charges is plotted on Figure 5: the carborundum (SiC) that is supposed to be an inert charge, the activated carbon and finally, the biomass char.

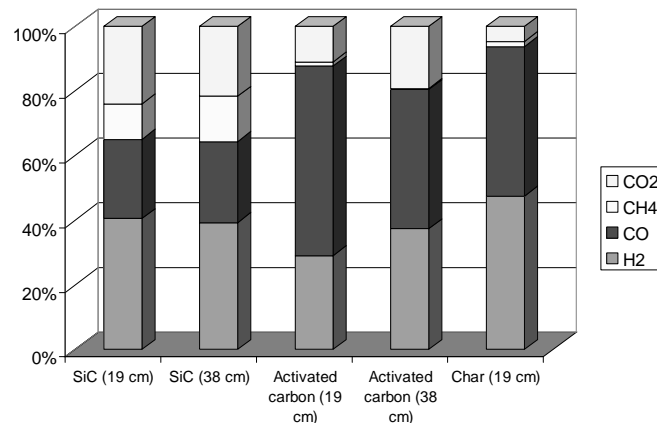


Figure 5: Gas composition at the exit of “PGTR” for different solids at 900°C.

To compare the three charges, their bed porosities are supposed to be identical.

First, we can see that activated carbon and biomass char act as catalysts because they increase the tar conversion and the conversion of methane and carbon dioxide compared with thermal conversion. We also obtained best results regarding tar degradation with activated carbon and biomass char.

By comparing activated carbon and biomass char, we can notice that hydrogen content is more important with biomass char and there are less carbon dioxide and carbon monoxide.

4.2.3. Residence time

For the carborundum and the activated carbon, two experiments were carried out with two different heights of bed, so two different residence times. The results are presented on Figure 5.

By comparing the residence time for SiC first, we can confirm that carborundum is inert and does not have any effect on the conversion of gas because the composition of gas is similar with or without the charge. For these tests, there is only a thermal effect.

For the activated carbon, increasing residence time the methane and carbon dioxide are more converted and therefore there are more hydrogen and carbon monoxide. For the test with higher height of bed, the rate of purification of methane and carbon dioxide are higher than 95 %. For the other test with a height divided by two, the concentration of carbon dioxide increases continuously, contrary to the methane. The assumption is that the methane is converted onto the activated carbon and the carbon dioxide is adsorbed. This assumption needs to be confirmed by performing adsorption and desorption isotherm experiments.

Regarding the tar, the use of activated carbon with the highest height of charge leads to a tar content lower than the system detection threshold that is near 1 g/Nm³. This explains the necessity of investigating the development of a quantitative analysis methods of the tar reaching very low threshold to achieve the specification expected for a use of syngas or pure hydrogen, i.e. a tar yield lower than 0,1 mg/Nm³.

4.3 Char as catalyst:

The loss of mass obtained during the use of the pyrolysis char in the “PGTR” is obtained by various phenomena: volatilization during the heat treatment undergone before test (heating of the carbonaceous residues during one night at 900°C), and the gasification of carbon during the test. It also depends on the carbonaceous compound deposit called soot or coke during the test. The share of gasified compound and deposit can only be approximated for the moment by using an assumption concerning the gasified part from thermogravimetric experiments and requires additional tests. Thus, a fractionated test is under preparation. In a first approach we can think that the volatilized mass would be near or lower than 15% that is the volatile matter content in the char at exit of pyrolysis. We can compare nevertheless the elementary compositions normalized on CHO of the three chars in Table 2 which are: the char resulting from biomass pyrolysis (char 1), the same residue that was having undergone a heat treatment (char 2) and this last having undergone a complete test (char 3).

Table 2: Elementary mass compositions of the three char: after pyrolysis, after thermal treatment and after the use in PGTR

	Char 1	Char 2	Char 3
C	90.45 %	98.80 %	99.27 %
H	3.00 %	0,35 %	0.43 %
O	6.55 %	0,79 %	0.3 %

It can be noticed that during the heat treatment the carbon content is more important, the product is impoverished out of oxygen and hydrogen. Then during the test, the tendency is still accentuated, the char is close to pure carbon in spite of the carbon loss by gasification. The hydrogen share being more important than in the case of the thermically treated char, we can pose the assumption that coke is not carbon pure but a CxHy mixture such as a PAH or that oxygen is released.

The decomposition of methane is close to that obtained by the activated carbon but the tar yield of the output is well far from the required specification of 0.1 mg/Nm³.

Thus, the use of the biomass char for the treatment of pyrolysis gas seems to be a possible way to improve quality of gas. But this result must be validated by further experiments and a more important mass of biomass char have to be charged to obtain an optimal conversion of the tar and methane.

5 Conclusions

To model the second stage of the process, the different products of the pyrolysis that are the reactants in the “PGTR”, the gas, tar and char are defined as well as the phenomena associated i.e. the gasification of the char, the reaction in gas phase, the water gas shift and the catalysed degradation of methane and the tar degradation reactions and interaction reactions in tar.

Eight “model compounds” were selected to represent the tar with respect to their reactivity and also with respect to the interactions related to the increase of the number of cycles.

In addition, experimental results on the “Biocarb” facility were obtained to better understand the phenomena. They show that a high temperature treatment improves the quality of the gas and that the activated carbon and char from biomass pyrolysis can be used as catalysts in order to the degradation of the methane and of the tar.

The next step of the study is to obtain kinetics of degradation of the tar and gasification of the biomass char on a smaller reactor like the high temperature tube using the “model compounds”. These experiments are ongoing. The final objective of this study will be the phenomenological model and the simulation of the “PGTR”, in order to be able to extrapolate the results obtained.

References

- AZNAR M.P., CABALLERO M.A., GIL J., MARTIN J.A., CORELLA J. (1998) Commercial steam reforming catalysts to improve biomass gasification with steam-oxygen mixtures. 2. Catalytic tar removal. *Ind. Eng. Chem. Res.* 37: 2668-2680
- BRAGE C., YU Q., CHEN G., SJOSTROM K. (2000) Tar evolution profiles obtained from gasification of biomass and coal. *Biomass and Bioenergy* 18: 87-91
- COURSON C., UDRON L., PETIT C., KIENNEMANN A. (2002). Grafted NiO on natural olivine for dry reforming of methane. *Science and technology of advanced Materials* 3: 271-283
- DEVI L., PTASINSKI K.J., JANSSEN F.J.J.G., VAN PAASENS V.B., BERGMAN P. C.A., KIEL J.H.A. (2005). Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renewable Energy*, 30: 565-587
- GUEHENNEUX G., GIMENO B.A., BAUSSAND P., JACOB V., KALUZNY P. (2002). Influence of sampling conditions on solid-phase microextraction for the extraction of gaseous polycyclic aromatic hydrocarbons. *Polycyclic Aromatic Compounds* 22: 537-547
- MARQUEZ-MONTESINOS F., CORDERO T., RODRÍGUEZ-MIRASOL J., RODRÍGUEZ J. J. (2002). CO₂ and steam gasification of a grapefruit skin char. *Fuel* 81: 423-429
- MILNE T. A., EVANS R. J., ABATZOGLOU N. (1998). Biomass gasifier “tars”: their nature, formation, and conversion. NREL/TP-570-25357. National Renewable Energy Laboratory, Golden, CO, 1998.
- PFEIFER C., RAUNCH R., HOFBAUER H. (2004) Hydrogen-rich gas production with a catalytic dual fluidized bed biomass gasifier. *Proceedings of 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection*, 10-14th May 2004, Rome, Italy
- SIMELL P., STÅHLBERG P., KURKELA E., ALBRECHT J., DEUTSCH S., SJÖSTRÖM K. (2000) Provisional protocol for the sampling and analysis of tar and particulates in the gas from large-scale biomass gasifiers. Version 1998. *Biomass and Bioenergy* 18: 19-38

Acknowledgments

We thank the French Agency for Environment and Energy Management (ADEME) for its financial support.